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ADSORPTION OF CHLORINATED HYDROCARBONS FROM SEAWATER BY A CROSSLINKED POLYMER

George R. Harvey

Woods Hole Oceanographic Institution

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Adsorption of Chlorinated Hydrocarbons from Seawater by a Crosslinked Polymer

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This report was submitted in fulfillment of project number 16020 GCQ under the sponsorship of the Office of Research and Monitoring, U. S. Environmental Protection Agency.

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ADSORPTION OF CHLORINATED HYDROCARBONS FROM SEAWATER BY A CROSSLINKED POLYMER

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SECTION I

CONCLUSIONS

1. Amberlite XAD-2 resin is an excellent adsorbant for hydrophobic chlorinated hydrocarbons dissolved in coastal and off-shore seawater.

2. Adsorbed compounds such as DDT and its metabolites, dieldrin and polychlorobiphenyls can be quantitatively eluted from the resin.

3. This resin has definite advantages over other solid sorbants now in use.

SECTION II

RECOMMENDATIONS

1. Amberlite XAD-2 resin should be the material of choice for monitoring coastal seawater for chlorinated hydrocarbon contaminants.

2. The resin should be evaluated for its adsorption properties toward petroleum hydrocarbons in natural waters.

SECTION III

INTRODUCTION

The objective of this work was to develop a working, analytical method for adsorbing and recovering low concentrations of chlorinated hydrocarbons (CHCs) such as pesticides and polychlorinated biphenyls (PCBs) from seawater using Amberlite XAD resins (Rohm & Haas Co., Philadelphia). The objective has been achieved and this report will describe this new analytical method.

The use of solid absorbants to concentrate CHCs, as well as other classes of chemicals of interest, has two significant advantages over the usual solvent extraction: 1. Very large volume samples are possible, i.e., 20-2000 liters, without any significant change in the apparatus; 2. The ratio of total water volume sampled to volume of solvent used for final isolation is very large. Thus, solvent impurities are minimized and the limit of detectability is reduced to ca. 1 part per trillion (ppt) or less.

When this work commenced only charcoal was in wide use as a solid absorbent for CHCs, in spite of the poor and variable recovery characteristics of this material (1). In addition, a short communication by Riley (2) described the use of Amberlite XAD-1 resin for adsorbtion of C^{14}-DDT from seawater. Unfortunately, only one liter was used in those experiments and no conditions were given. We believed that the resin had promise as an analytical tool, but an analytical method had to be researched. The research presented in this report substantiates that belief.

While this work was in progress, two other adsorption methods for seawater became available: Reversed liquid-liquid partition chromatography (3), and the use of polyurethane foam (4). Both of these methods have disadvantages which restrict its use to particular applications. The method described in this report should be of general applicability and usefulness.

We originally intended to develop a method for the DDT family, Dieldrin, Chlordane, etc. in seawater. However, it soon became obvious that the major CHCs in coastal New England waters were PCBs. Thus, we were forced to evaluate the resin against those compounds, as well as the pesticides.

SECTION IV

EVALUATION

General Characteristics of Amberlite XAD-2 Resin (XAD-2), (5)

XAD-2 is a synthetic polymer of styrene and divinyl benzene which is further crosslinked and formulated into 20-50 mesh white beads. The surface area is 300 m^2/g and the mean pore diameter is 85-95 Å. It is heat stable to at least 200°C. On one occasion we lowered several grams of XAD-2 to 1000 m in the sea and observed no compression of the beads. This property will allow the resin to be used in in situ sampling pumps lowered to the desired depth. This is a major advantage over polyurethane foam which is highly compressible. For the present objectives the most valuable property of XAD-2 is its ability to adsorb dissolved hydrophobic compounds from water, presumably by hydrophobic bonding which is thermodynamically favored by the entropy increase in the water.

Cleanup of Resin

The commercial product, as received, is very contaminated and contains PCBs, as well as other materials. After much experimentation the following procedure was adopted:

1. Wash resin with several portions of tap water by slurrying and decanting.

2. Put resin in a metal container having a 60 mesh screen bottom and wash out the fines with 20 bed volumes of tap water, followed by a distilled water rinse.

3. Extract the resin in a Soxhlet apparatus with pesticide grade acetonitrile for 18 hours. Change the solvent and repeat for another 18 hours.

4. Rinse the resin free of acetonitrile with ten bed volumes of distilled water.

5. Store the resin in tightly sealed glass jars covered with distilled water until use.

Large batches can be prepared in this way. It need not be repeated after using the resin since the elution procedure is sufficient for immediate re-use.

Adsorption of Total Dissolved Organic Carbon

Falmouth seawater, containing 2.1 mg/l of dissolved organic carbon was run through an 8 cc bed of resin at flow rates of 1.4, 0.7, 0.3 and 0.1 bed vol/min. The effluent at the first three flow rates had 1.7, 1.4 and 1.3 mg C/l, or about 80%. At the low flow rate the resin saturated after one liter indicating secondary adsorption. These preliminary results led to two valuable conclusions:

1. Coastal seawater contains about 20% hydrophobic organic matter.

2. At higher flow rates the resin will preferentially adsorb only hydrophobic material from water, while at low flow rates discrimination is lost and all the organic matter is adsorbed causing the resin to saturate prematurely.

Preparation of Spiked Seawater Solution

Unfiltered, Falmouth seawater (19 liters) was spiked with acetone solutions of DDT, DDE, Dieldrin and PCB (Aroclor 1254) to a concentration of 5-10 ppb. The water was stirred for 48 hours before vacuum filtration through a 0.3 μ glass fiber filter. An aliquot of the filtered water was extracted with 6% ether in hexane and analyzed by gas liquid chromatography (glc). The resulting concentration was generally between 1 and 3 ppb. The major portion of the chlorinated hydrocarbons remained on the filter. These spiked solutions were used to evaluate many of the parameters of the analytical system. However, the concentrations varied daily in an irregular manner, leading to many erroneous conclusions. Therefore, the final testing of parameters was done with unspiked seawater using the ambient levels of these materials (10-30 parts per trillion PCB, 1-4 ppt DDT) as determined by solvent extraction.

Capacity of XAD-2 for Chlorinated Hydrocarbons

Saturation of the resin with chlorinated hydrocarbons was never achieved, however, the capacity of the resin is large enough to be of no concern for large volume sampling. For example, seawater solution containing 1.6 ppb DDE, 3.1 ppb dieldrin and 2.3 ppb DDT was passed through a 5 cc column of resin at 5 ml/min gravity flow. After 65 liters had passed the column clogged, although adsorption was still efficient. Elution with 20 ml of acetonitrile gave recoveries of 125, 108 and 92 percent. This amounts ot 70 μg/cc of resin. When a pump was used to run the column no reduction in flow rate was observed, even after 100 liters. As a safety margin we have used no more than 13 liters

of seawater per cc of resin. This is clearly not a serious restriction.

Column Dimension

By using a constant volume of resin (5 cc) and varying the dimensions of the cylindrical column (length/i.d.) we were able to measure the percent bleed of DDE at a flow rate of 10 ml/min. The percent bleed, at l/i.d. = 7, was 9 and increased as the l/i.d. ratio increased to 24% at l/i.d. - 122. The longer columns are clearly less efficient and we recommend a column of l/i.d. = 7.

Optimum Flow Rate

Seawater spiked with one ppb of PCB and DDT was passed through several 10 cc columns of XAD-2 (l/i.d. = 7) at different flow rates. A total of five liters was passed through each column, followed by 40 cc of acetonitrile for elution. The results are shown in Figure 1. Five bed volumes per minute is the maximum flow rate for complete adsorption of the chlorinated hydrocarbons. The slightly lower efficiency at two bed vol/min is probably due to the phenomenon discussed in General Characteristics of the XAD-2 Resin.

The above parameters were checked by passing several liters of Woods Hole seawater through the same columns at five bed vol/min, eluting and quantifying. The results were compared several times with solvent extraction of the same water (6% ether-hexane). In all cases the results were the same, i.e., the same quantity of DDT, Dieldrin and PCB by either method, usually 4, 10 and 30 ppt respectively.

Elution and Regeneration

In preliminary experiments and from theoretical considerations it was obvious that a water miscible organic solvent was required for penetration of the wet resin. Acetonitrile and ethanol were evaluated and found to be quite satisfactory. Four bed volumes of either solvent is passed through the resin at 0.2 bed vol/min. After two bed vol. more than 90% of the chlorinated hydrocarbons have been eluted. An alternate method is to pour four bed vol. of either solvent, boiling hot, through the resin at full gravity flow. Recovery in both cases is 100%. The solvent is washed off the column with four bed vol. of water and the column is ready for the next sample. We have reused the same column 15 times with no change in its efficiency.

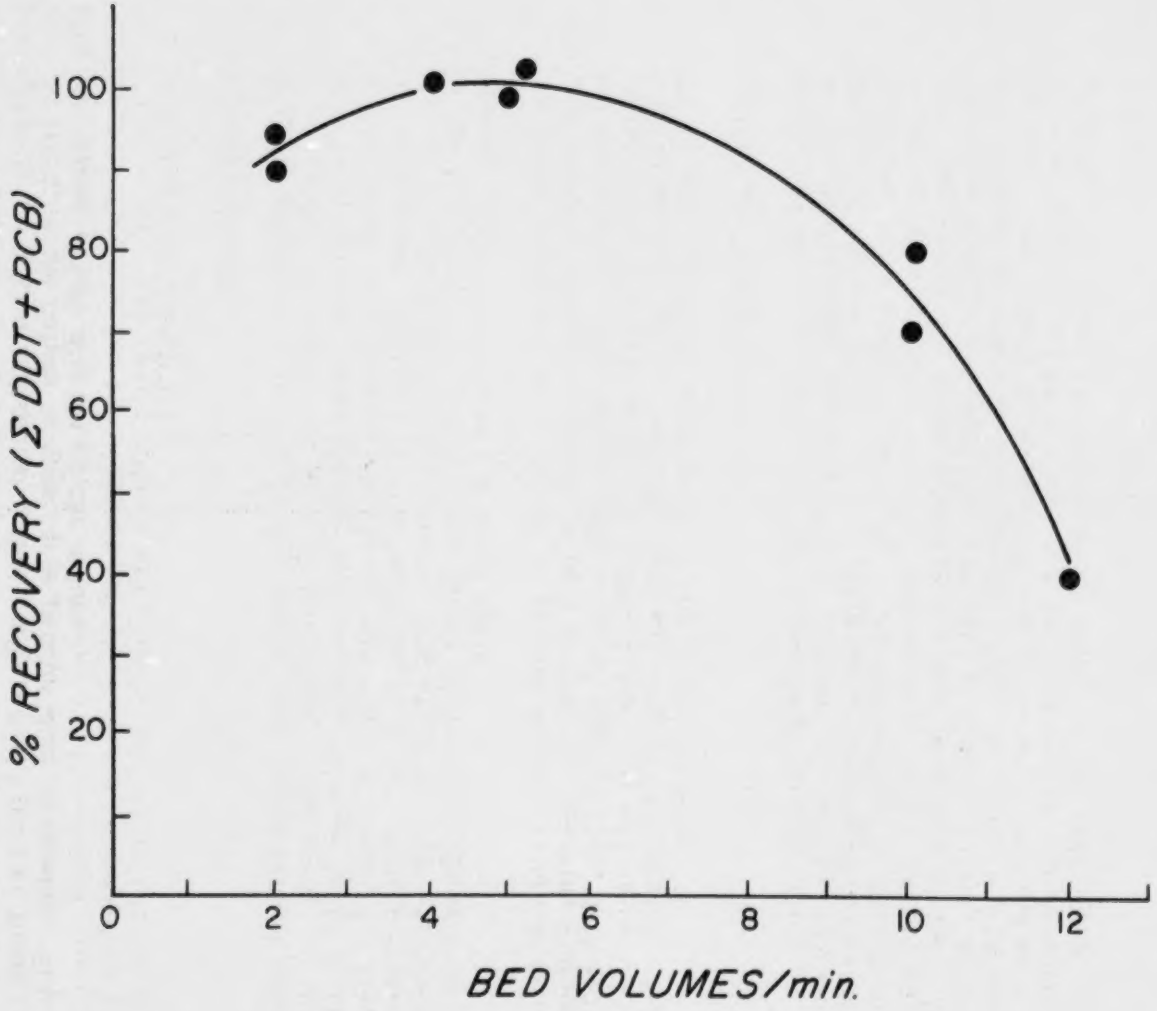

Figure 1. XAD-2 Column Efficiency

Prefiltration

Amberlite XAD-2 resin can adsorb only from the dissolved phase. Chlorinated hydrocarbons adsorbed on particulate matter smaller than 20 mesh will pass through the column undetected. Thus, only a small plug of glass wool in front of the column to trap large particulates is needed. This plug is removed before elution of the column.

SECTION V

EXPERIMENTAL

Reagents	Preparation
Amberlite XAD-2 resin (supplied by Eastman Kodak)	See Evaluation - Section A
Acetonitrile	Pesticide grade, or reagent grade redistilled in all glass still
Ethanol	CSI pharmaceutical grade
Hexane	Pesticide grade, or reagent grade redistilled from sodium metal in all glass still
Water	Distilled or pre-analyzed tap or seawater
Glass Wool	Heat at 350^{o} for 48 hours in vented oven and store in glass jars.
Sodium Sulfate	Anhydrous reagent, treated as glass wool.

Apparatus

A suggested apparatus is diagrammed in Figure 2.

Procedure

A brass or glass column is packed with a 50 cc bed of XAD-2 resin and fitted with a 5 cm pre-column of glass wool (Fig. 2). Seawater is pulled through the column with a peristaltic pump at a rate of 250 ml/min until 20 to 100 liters have been extracted. The pre-column or filter and other fittings are removed. Hot acetonitrile or ethanol is poured through the column (200 ml) at full gravity flow into a 1 liter separatory funnel fitted with a Teflon stopcock. Water (500 ml) is poured through the column into the same separatory funnel. The column is now ready for immediate re-use. The aqueous acetonitrile or ethanol (700 ml) is extracted with 2 x 50 ml of hexane.

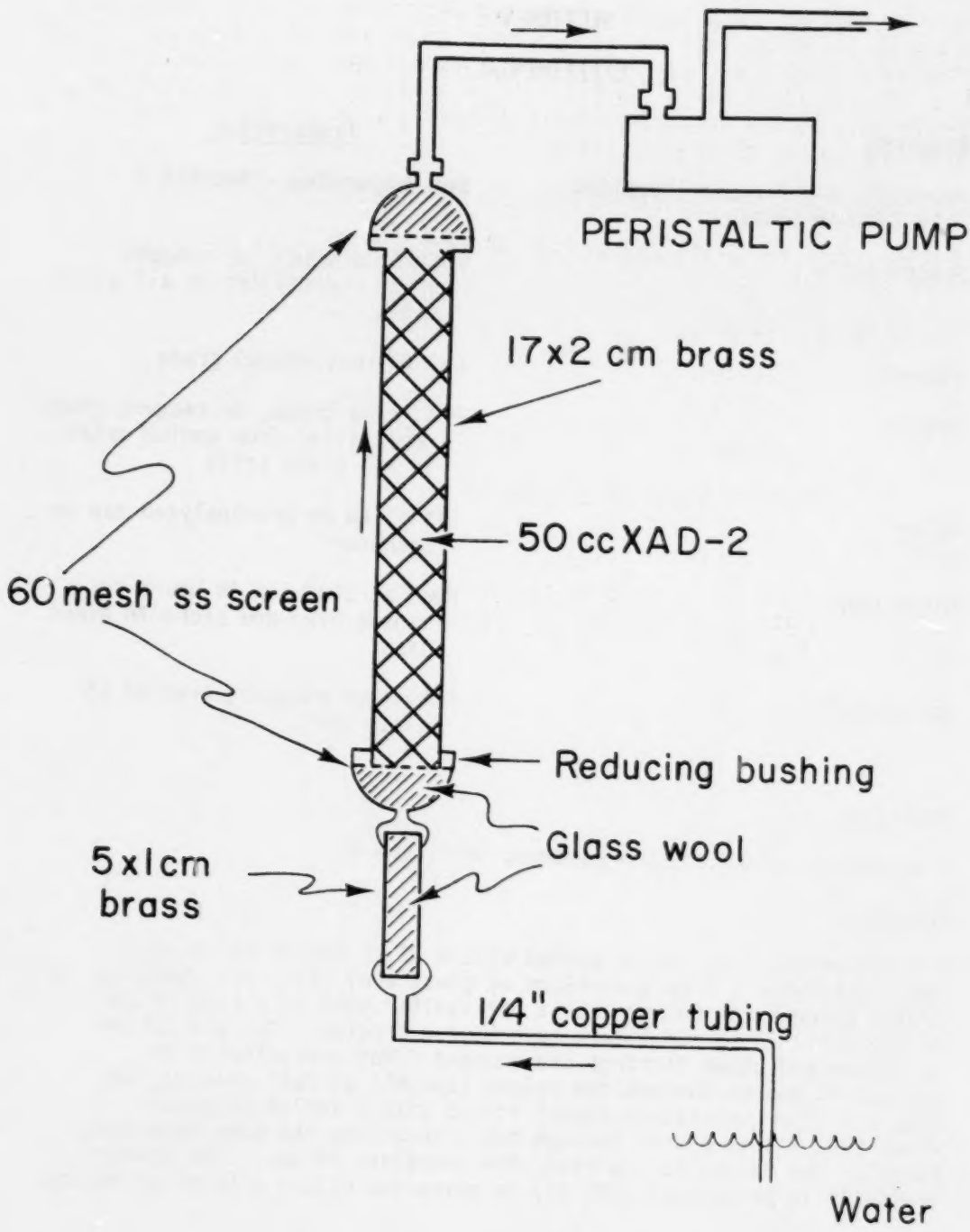

Figure 2. Adsorption Apparatus for 20-100 Liters of Seawater

The combined hexane extracts are washed with 25 ml of water, dried with 3-5 g of sodium sulfate and concentrated to an appropriate volume for gas chromatographic analysis, or silica chromatographic separation of PCB from the DDT family (6). No florisil or sulfuric acid cleanup of the hexane extract was necessary before gc analysis in our work including both inshore and open-ocean seawater.

Gas Chromatographic Conditions Used in This Work

Column: 2m x 2mm glass packed with 8% QF-1 and 2% OV-17 (1:1) on Anakrome (100 - 120 mesh).

Temperatures:	Injector	-	240°
	Column	-	190°
	Manifold	-	220°
	Detector	-	250°

Gas: 5% methane in Argon at 40 ml/min.

Detector: Ni-63 in pulse mode.

Any standard methods for separation of the pesticides from the PCB's and their quantitation can be used (6). Some typical results are shown in Table 1 and Appendix 1.

SECTION IV

DISCUSSION

Amberlite XAD-2 resin, as described in this report is an excellent adsorbent for chlorinated hydrocarbon contaminants in seawater. The resin should work quite well with freshwater, but the "salting out" effect of seawater probably makes the high flow rates possible. XAD-2 resin has two advantages over polyurethane foam (4) and reversed phase liquid-liquid chromatography (3). Firstly, there is no organic coating on the XAD-2 so that after elution of the column it is ready to be reused. Secondly, the XAD-2 has excellent pressure resistance, so it can be used in in situ columns at depth. We have tested XAD-2 at 1000 m and observed no compression of the spheres.

The system described in this report should be sufficiently flexible for any natural water monitoring of ambient levels of chlorinated hydrocarbons. In connection with another project, we have used XAD-2 resin to monitor the water of the open - North Atlantic Ocean (Table 1, Appendix 1). In that work 20 - 80 liters of seawater was pumped through the 50 cc column described here. The efficiency of the column was checked several times by simultaneous solvent extraction and was found to be >95%.

The column conditions described in this report were given to Drs. Donald C. Gordon and Rodney A. Badger of the Bedford Institute of Oceanography, Marine Ecology Laboratory, Dartmouth, Nova Scotia. They evaluated our parameters by using C^{14} labelled DDT. They found the resin to be 97.5% efficient at a flow rate of 5 bed volumes/min. and the recovery was 100%. These results will not be published and are mentioned here as an independent confirmation of our observations.

One use of the resin which should be exploited for coastal monitoring is in situ sampling from a ship underway. If a flow meter was attached to a weighted column set in a "fish" it could be towed while other work was in progress. Furthermore, a more representative, or integrated sample would be obtained.

TABLE 1

TYPICAL PCB AND ΣDDT IN WOODS HOLE SEAWATER BY XAD-2 ADSORPTION

Date	(PCB)[a]	(ΣDDT)[a]	Volume (ℓ)
4-7-72	7.1	<.1	4
4-13-72	10.3	0.7	4
5-4-72	b	1.3	4
5-11-72	b	3.3	4
6-14-72	b	3.3	18.5
10-4-72	35	0.3	12
11-14-72	7.2	2	96[c]

a) Reproducibility is ± 10%; verified by ether-hexane extraction. Values given in parts per trillion.

b) Not calculated due to very poor chromatographic matching with standard, commercial PCB mixtures.

c) By immersion of water intake tube below the surface of the sea at the Woods Hole dock.

SECTION VII

ACKNOWLEDGEMENTS

The analytical, mechanical and intellectual efforts to this work by Mr. William G. Steinhauer have been major, and they are responsible for the success of the project.

Without the generous support of the Office of Research and Monitoring, Environmental Protection Agency, this work would have been impossible. The assistance of Dr. Earl Davey, Project Officer is appreciated.

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1. Breidenback, A. W., et al., The Identification and Measurement of Chlorinated Hydrocarbon Pesticides in Surface Waters, Federal Water Quality Administration, No. WP-22, Gov't. Printing Office, Washington, D. C., 1966.

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3. Ahling, B. and S. Jensen, Reversed Liquid-Liquid Partition in Determination of PCB and Chlorinated Pesticides in Water, Analytical Chem., 42, 1483 (1970).

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GLOSSARY

DDT or ΣDDT - The family of the pesticide DDT and its major metabolites, DDD and DDE.

PCB - The class of industrial chemicals composed of a mixture of polychlorinated biphenyls.

Chlorinated Hydrocarbon - Any organic compound composed of only carbon, hydrogen and chlorine.

Amberlite - A trademark of Rohm and Haas Co., Philadelphia, Pa. for their class of exchange resins.

APPENDIX 1

POLYCHLOROBIPHENYLS IN NORTH ATLANTIC OCEAN WATER

by

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Abstract

Concentrations of polychlorobiphenyls (PCBs) have been measured in the water of the North Atlantic Ocean from surface and various depths between 26^{o} and 63^{o} North latitude. The concentrations average twenty parts per trillion and amount to an estimated 2×10^{4} tons of PCB in the upper 200 m. The surface water of the Sargasso Sea contains average PCB concentrations which are lower than the northern North Atlantic.

Seawater is the most abundant solvent available for trapping hydrocarbons, such as the PCBs, released into the environment. The volume of the oceans (10^{21} liters) is sufficient to dissolve all the PCBs which have been made (1). Relatively few PCB measurements have been made in open-ocean water to determine the extent to which it functions as a solvent trap (2). Most analyses have been confined to organisms (3) which comprise less than 1 ppm of the total volume.

During the summer of 1972 we analyzed open-ocean water from the eastern and western North Atlantic between 26°N and 63°N. The stations are marked in Figure 1 and the analyses are tabulated in Table I (4). Samples 1 to 9 and 13 were analyzed by extracting 19 liters of seawater (5) with 6% ether-hexane, followed by concentration and electron capture gas chromatography (ECGC). The other samples were analyzed by pumping 19 to 80 liters of water through a 50 cc brass or glass column (length/-diameter = 6) of Amberlite XAD-2 resin (6) at 250 ml/min. The PCBs were eluted from the column with 300 ml of hot acetonitrile at full gravity flow. The acetonitrile was diluted with one liter of water (distilled or seawater) and extracted with hexane. The hexane was treated as above. It was found that no cleanup of the extract was required prior to ECGC. Unfiltered seawater samples collected and analyzed simultaneously with water filtered through a 0.3 μ glass fiber or a glass wool plug revealed a maximum of 10% more PCB. All analyses were completed on shipboard within four hours of sampling (7).

Three observations can be made from the data:

1. Concentrations of PCBs in the northern North Atlantic average 35 ng/kg (ppt) in surface waters, and 10 ppt at 200 m.

2. PCB concentrations do decrease with depth.

3. The surface waters of the Sargasso Sea have slightly lowered surface levels of PCBs (27 ng/kg) than other parts of the North Atlantic.

The widespread distribution of PCBs in the open-North Atlantic supports previous observations that the atmosphere must be the predominant mode of transport (3). The wide range of concentrations observed (< 1-150 ppt), in some cases only 50 miles apart (Stations 29 and 33), may be due to sea slicks (2), localized rainfall or discharges from other ships. No relationship between PCB concentration and proximity to land was observed. The presence of measurable PCB concentrations, even to 3000 meters, suggests that animals which migrate vertically, plus sinking shells, feces and dead organisms transport PCBs out of the mixed layer (ca. 150 m) and prevent even higher concentrations from accumulating in the productive zone.

The Sargasso Sea is an area of high evaporation and low rainfall. We suggest that PCBs, adsorbed on particulates falling into this region, are partially solubilized by equilibrating with the surface water. Evaporative codistillation then transports some of this material to areas of higher precipitation.

The volume of the upper 200 m of the North Atlantic is 10^{18} liters. If we assume an average PCB concentration of 2×10^{-8} g/l in that volume (8) then there is about 2×10^{10} g (2×10^{4} tons) in the water (1, 9). In 1971 the U. S. manufactured 1.8×10^{4} tons (1). Thus, a considerable fraction of the world's 40 year production has been trapped by the North Atlantic Ocean.

Finally, based on quantitative estimates of production and rates of losses to the environment a ΣDDT/PCB ratio of 10 is expected in the North Atlantic, assuming similar half lives (9). The observed ratio from our data (and Reference 2) must be less than 0.05 (footnote b, Table I). Thus, the environmental half life of the PCBs appears considerably greater than the DDT family.

TABLE I[a]

Concentrations of PCBs in North Atlantic Ocean Water

Station	Position North deg.	min.	West deg.	min.	Date (1972)	Depth (meters)	PCB (x 10^{-9} g/l)[b]
1	52	55	35	08	6/30	0	150
2	44	00	30	36	7/3	0 - 200	35 - 10
3	40	33	29	16	7/5	0 - 200	4 - 7
4	36	11	25	33	7/7	0 - 200	11 - 3
5	34	02	22	50	7/9	0 - 200	30 - 6
6	35	00	18	59	7/11	0 - 200	14 - 5
7	34	47	14	57	7/13	0 - 200	67 - 39
8	38	20	11	23	7/15	0 - 200	19 - 2
9	38	23	11	11	7/22	0 - 200	41 - 13
10	38	19	19	28	7/23	0	77
11	41	09	20	46	7/24	0	< 1
12	43	57	22	13	7/25	0	52
13	43	20	21	57	7/27	0	47
14	43	16	21	34	7/29	100 - 3000	> 1[c]
15	46	31	21	43	7/30	0	10
16	52	31	19	52	8/1	0 - 100	45 - 8
17	52	35	19	53	8/2	1500	> 1[c]
18	55	41	15	02	8/4	0	3
19	57	22	12	01	8/5	200	97
20	60	04	06	02	8/6	200	42
21	60	09	05	36	8/7	0	82
22	60	29	04	43	8/7	0	23
23	63	03	02	22	8/8	0 - 200	21 - 7
24	41	32	70	40	10/2	0	30
25	39	40	70	03	9/21	0	29
26	37	12	68	54	9/22	0	36
27	34	32	67	01	9/23	0	12
28	35	22	67	36	9/24	1000	1
29	35	17	68	28	9/24	0	2
30	35	56	66	34	9/25	0	5
31	36	05	67	27	9/26	0	11
32	36	24	68	24	9/27	0	22
33	35	37	67	49	9/27	0	9
34	34	26	66	22	9/28	0	12
35	33	41	65	44	9/28	0	15
36	28	42	58	39	10/3	0	26
37	26	50	55	38	10/5	0	36
38	25	56	54	15	10/6	0	27
39	26	58	53	57	10/7	0	42
40	28	26	53	55	10/8	0	88
41	31	13	53	49	10/9	0	68

(Table I Continued)

a) The limit of detection was 1×10^{-9} g/l for a 19 liter sample.

b) The closest matching commercial mixture in all cases was that containing 54% chlorine. Aroclor 1254 (Monsanto Company) was used as the standard. Procedural blanks ranged from 0 - 3 ng/l and were subtracted from the tabulated concentrations. The DDT family, if present, was at concentrations less than 1 ng/l.

C) Poor match for Aroclor.

References and Notes

1. The total U. S. production of PCBs since 1957 is about 3.6×10^{11} g (data released by Monsanto Company, November 1971) which is estimated to be about one-half of the total world production.

2. Olney, C. E. and J. G. Quinn in: Deliberations of the International Decade of Ocean Exploration Baseline Conference, E. D. Goldberg, convener, Scripps Institution of Oceanography. May 24-26, 1972. These workers made PCB measurements in the surface microlayer and from 20 cm below the surface in the North Atlantic. Their subsurface concentrations agree with our surface measurements, although their sample size was much smaller.

3a. Harvey, G. R., V. T. Bowen, R. H. Backus and G. D. Grice in: Nobel Symposium 20: The Changing Chemistry of the Oceans, D. Dyrssen and D. Jagner, Eds., Almquist and Wiksell, Stockholm, 1972, p. 177.

3b. Deliberations of the International Decade of Ocean Exploration Baseline Conference, E. D. Goldberg, convener, Scripps Institution of Oceanography. May 24-26, 1972.

4. Stations 1 to 23 were occupied on cruise 105 of R/V CHAIN; Stations 25 to 41 were occupied on cruise 71 of R/V ATLANTIS II. Station 24 is the Woods Hole dock.

5. Surface samples were collected in a stainless steel bucket from the bow of the ship underway. Deep samples were collected in a 120 liter Niskin-type bottle lined with Teflon.

6. Rohm & Haas Co., Philadelphia. The given parameters for using this resin were developed by the authors in this laboratory. The efficiency of the adsorptive extraction, when compared with solvent extraction, is >95%.

7. A Packard gas-liquid chromatograph, model 407, equipped with a Ni-63 electron capture detector was used. No motion sensitivity was observed in the instrument's response. The ship's paints, greases and oils did not contain any PCBs as determined by shipboard analysis.

8. These data and Reference 2. In contrast, PCB concentrations in coastal northeast Pacific waters average 1 ppt (I. Barrett in Reference 3b).

9. This quantity is remarkably similar to a recently calculated estimate of PCBs in the N. Atlantic as 1.5×10^4 tons. No water data was available at the time of the calculation. I.C.T. Nisbet and A. F. Sarofim, Environmental Health Perspectives, 1, 21 (1972).

10. We thank Dr. R. H. Backus, chief scientist on R/V CHAIN-105 for the opportunity to collect those samples and Dr. V. T. Bowen for making the deep samples available. Supported by NSF Grant GX 35212, Office of the International Decade of Ocean Exploration, and EPA grant GQ 16020.

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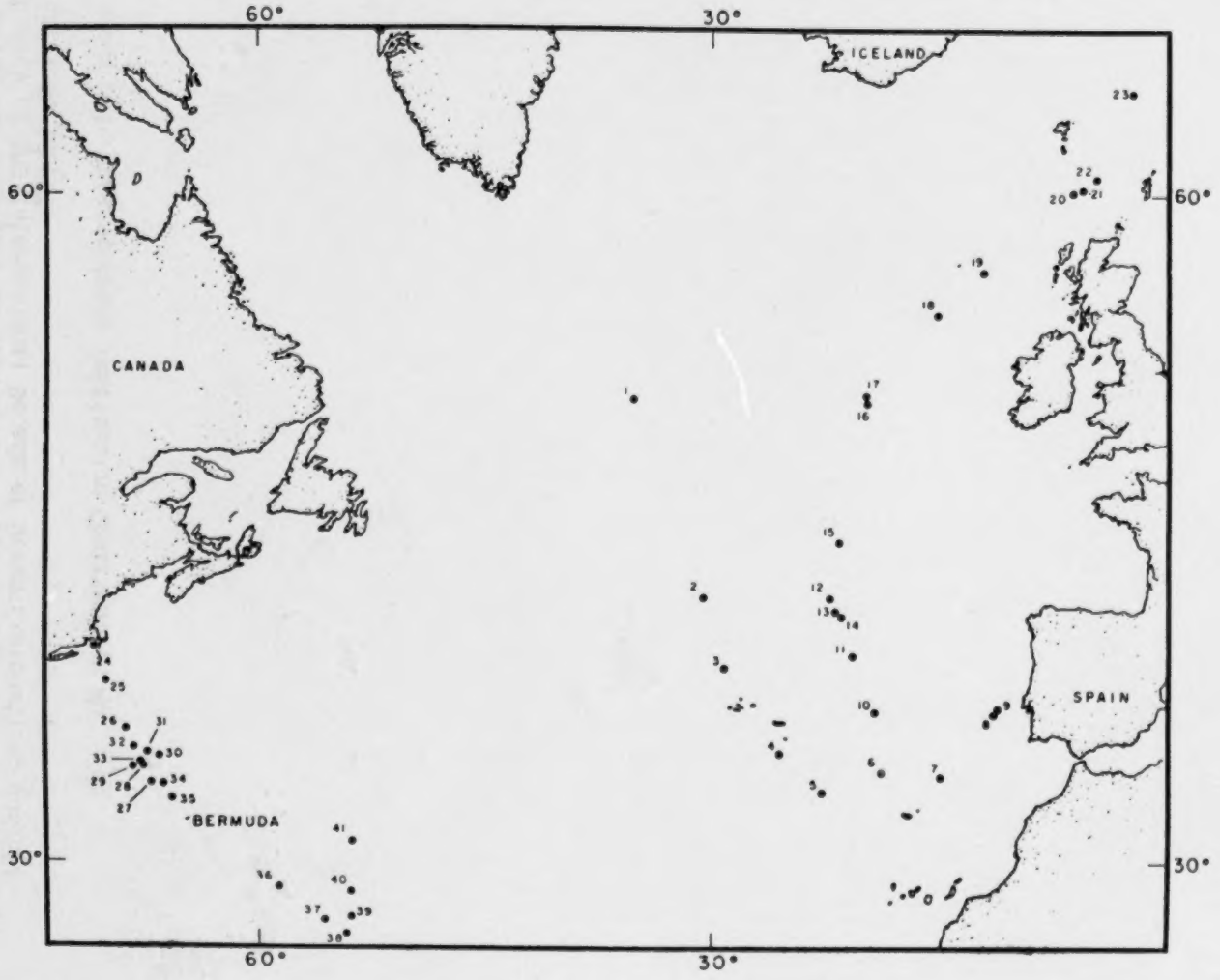
Figure 1. Water Station Locations in the N. Atlantic Ocean



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